



Reduction of NO_x over a combined NSR and SCR system

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ABSTRACT

Flow reactor experiments are performed over a model Pt/Ba/Al catalyst, an Fe-beta sample, and over a combined system where the Pt/Ba/Al catalyst is placed upstream the Fe-beta sample. The combined system show a superior NO_x removal efficiency and a lower ammonia slip compared to the single Pt/Ba/Al catalyst at all temperatures examined. Ammonia, formed during the rich period over the Pt/Ba/Al, is stored in the SCR catalyst and consumed in the following lean period which results in a decrease of the NH₃ slip and an increase of the NO_x removal efficiency. The optimum temperature for NO_x removal of the combined system is 300 °C; at this temperature a remarkably high NO_x removal efficiency of 99.5% is achieved. The SCR catalyst exhibit a high ammonia adsorption capacity at 200 °C which results in a very low NH₃ yield (3%) and a high N₂ yield (85%) for the combined NSR and SCR system. There is a benefit when NO₂ is present in the feed at low temperatures. The NO_x removal efficiency of the combined system increases due to the increase in the amount of NO_x stored over the Pt/Ba/Al sample. Furthermore, the amount of NO_x removed over the combined system is influenced by the amount of hydrogen in the rich periods. A higher hydrogen concentration enhances the NO_x removal efficiency at lower temperatures. At higher temperatures an optimum hydrogen concentration exists due to ammonia inhibition of the SCR reaction when an excessively high H₂ concentration is used.

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1. Introduction

The use of diesel engines and lean-burn gasoline engines decreases the fuel consumption and thereby reduce the emissions of CO₂. However, due to the large excess of oxygen during the operation of these engines, nitrogen oxides cannot be reduced over the conventional three-way catalyst. Since nitrogen oxides have devastating effects on the environment as well as on the human health, it is of utmost importance to decrease the NO_x emissions. Two catalytic concepts that can reduce NO_x from lean exhaust gases are the NO_x storage and reduction (NSR) and the urea-SCR techniques. In the urea-SCR concept urea is injected into the exhaust gas and is decomposed into ammonia which selectively reacts with NO and NO₂ over the catalyst and produce N₂ [1]. The NSR technique reduces NO_x emitted from lean-burn engines by storing NO_x in the catalyst during lean operation. In order to retain the storage capacity of the catalyst, it has to be regenerated periodically from the NO_x stored. This is done during short rich periods, where the exhausts are oxygen deficient. During the rich conditions the NO_x

adsorbed is released and reduced into N₂ and possibly undesired by-products [2]. A typical NSR catalyst contains a high surface area support (such as γ-alumina), storage components (usually alkali or alkali-earth metal compounds such as barium or potassium), and precious metals (commonly Pt, Pd or Rh).

The reduction of NO_x by hydrogen over NSR catalysts has obtained a lot of attention recently and especially the formation of the by-product ammonia [3–8]. Abdulhamid et al. [3] showed that the selectivity to NH₃ under rich conditions was higher for catalysts containing Pt and Pd than Rh-containing catalysts. The formation of NH₃ depends on the feed composition; and ammonia is observed when the H₂/NO ratio is high [4–6]. The presence of oxygen in the regeneration feed also influences the amount of ammonia formed [9]. In addition, the temperature affects the amount of ammonia produced during rich conditions. Xu et al. [6] showed that the ammonia formation is favored for high H₂/NO ratios and at intermediate temperatures (100–350 °C). If the length of the rich period is short the selectivity to N₂ is usually high. However, if the rich period is extended, ammonia is observed if enough hydrogen is present in the feed [10]. Recently, Clayton et al. [9] showed that the Pt dispersion significantly affects the product selectivity and thereby the ammonia formation during rich conditions. Furthermore, several groups have proposed that ammonia formed during rich conditions may further react with the NO_x species adsorbed [4,5,7,8,10–12] and it has also been proposed that NH₃ is equally

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efficient as a reducing agent as H_2 [4]. We have developed a detailed kinetic model of NO_x storage and reduction with hydrogen [11]. The mechanism is based on experimental results [10,13] and contains ammonia formation, ammonia oxidation and reactions between adsorbed NO_x species and ammonia. The reactions between NH_3 and NO_x were crucial in order to describe the rich conditions and the outlet ammonia concentration from the Pt/Ba/Al catalyst is well described by the model.

The desired product of the reduction of NO_x over NSR catalysts is N_2 . However, the formation of ammonia over the NSR catalyst can be used as an advantage if an SCR catalyst is placed downstream an NSR catalyst. The ammonia formed over the NSR catalyst during rich conditions can then be stored on the SCR catalyst. In the following lean period the ammonia adsorbed is consumed over the SCR catalyst by NO_x that was not trapped by the NSR sample. Hence, a lower amount of both NO_x and NH_3 will be emitted from this catalyst configuration. Only a few studies are available which investigate the combined NSR and SCR system [14–19] and the general conclusion is that the NO_x removal efficiency is enhanced when a combination of NSR and SCR catalysts is used. Forzatti and Lietti [15] confirmed the occurrence of the SCR reaction by observing N_2 during lean conditions over a Pt–Ba/Al₂O₃ and Fe-ZSM-5 catalyst combination. Corbos et al. [17] investigated the combination of Pt–Rh/Ba/Al₂O₃ together with either Cu-ZSM-5, Co–Al₂O₃, or Ag/Al₂O₃ and they showed that the catalyst configuration with Pt–Rh/Ba/Al₂O₃ physically mixed with Cu-ZSM-5 had the highest activity. Moreover, Nakatsuji et al. [14] developed a catalyst composed of a noble metal supported on an oxygen storage material as a bottom layer and a solid acid as top layer. The bottom layer adsorbs NO_x and produces NH_3 during regeneration and the top layer is optimized for high NH_3 storage capacity. However, there are no studies available which investigate the effect of hydrogen concentration and NO_2 to NO_x ratio on the combined NSR and SCR system. Further, there are no results reported concerning NSR and SCR system using an Fe-beta catalyst.

In this work the combined NSR and SCR system is investigated in more detail and more specifically the effects of changing the NO_2 to NO_x ratio and the hydrogen concentration are studied. For this purpose flow reactor experiments are performed over a model Pt/Ba/Al catalyst and over the combined system where the Pt/Ba/Al catalyst is placed upstream the SCR catalyst. Lean/rich cycling experiments over all catalyst configurations are performed at different temperatures in order to clarify the role of the individual catalysts in the combined system. In addition, the effect of the NO/NO_2 ratio in the feed as well as the influence of the hydrogen concentration on the performance of the combined NSR and SCR system is investigated.

2. Experimental

2.1. Catalysts

The catalysts examined in this study are a Pt/Ba/Al catalyst used for the NSR process and an Fe-beta sample used for the SCR process. Both catalysts are monolith samples. The Pt/Ba/Al catalyst has a cell density of 400 cpsi; the length is 30 mm and the diameter is 21 mm. The washcoat weight of the sample is 1040 mg and it contains 2.9 wt% Pt and 20.8 wt% Ba. The catalyst was prepared by first wash-coating a cordierite monolith with γ -alumina, which was followed by incipient wetness impregnation of platinum. Barium was added to the sample after the Pt impregnation. The Pt precursor used was $Pt(NO_3)_2$ and the precursor used for barium was $Ba(NO_3)_2$. The preparation method is described in detail in [10]. Characterization of the Pt/Ba/Al catalyst was performed after the preparation procedure and before any activity measurements (i.e. when the catalyst was fresh). The specific surface area of the sample, which was determined by nitrogen adsorption at 77 K according to the BET method,

was $97\text{ m}^2/\text{g}_{\text{washcoat}}$. The instrument used for measuring this was a Micromeritics ASAP 2010. The Pt dispersion measured after the preparation procedure was 18%. The method used for measuring Pt dispersion was N_2O dissociation performed in a reactor equipped with a mass spectrometer (Balzer QME 125) [20]. The SCR catalyst used in this work is an Fe-beta catalyst provided by Haldor Topsoe A/S. It contains 1.4 wt% Fe. The length of the monolith is 22 mm and the diameter is 21 mm.

2.2. Activity measurements

The experiments conducted in this study were performed in a flow reactor consisting of a horizontal quartz tube with an insulated heating wire. The total flow rate used in all measurements was 3500 ml/min and argon was used as the carrier gas in the experiments. All gases were introduced by mass flow controllers (MFC) and a CEM-System (Controlled Evaporation and Mixing) from Bronkhorst was used to control the flow of water. Activity measurements were performed either over the Pt/Ba/Al catalyst or over the Fe-beta catalyst or over the combined system where the Pt/Ba/Al catalyst was placed upstream the Fe-beta catalyst. Two thermocouples were used to measure and control the temperature. One thermocouple was placed about 10 mm in front of the catalyst and the other was placed inside the catalyst, 10 mm from the rear end in the measurements performed over the single Pt/Ba/Al catalyst and the single Fe-beta catalyst. When experiments were performed over the combined system one thermocouple was placed inside the downstream catalyst (i.e. in the Fe-beta sample) and the other thermocouple was placed between the two samples (11 mm in front of the Fe-beta catalyst).

The outlet gas concentrations were analyzed by a MultiGasTM 2030 HS FTIR instrument. Before every experiment the samples were pretreated at 500 °C with 10 min of 8% O_2 in Ar followed by 5 min of 100% Ar. Finally the samples were reduced in 1.8% H_2 for 10 min. Lean/rich cycling experiments were conducted at 200 °C, 300 °C and 400 °C over the catalysts. The composition of the lean gas mixture was 300 ppm NO , 8% O_2 , 3% CO_2 and 3% H_2O and during rich conditions the feed contained 300 ppm NO , 16,000 ppm H_2 , 3% CO_2 and 3% H_2O . Ten lean/rich (4 min/1 min) cycles were performed in each experiment. When nothing else is stated the results from the three last cycles are shown throughout this paper. Experiments with either 300 ppm NO_2 or 150 ppm NO and 150 ppm NO_2 as NO_x source were also investigated. Moreover, the effect of the hydrogen concentration was studied and three different hydrogen concentrations were investigated: 2000 ppm H_2 , 8000 ppm H_2 , and 16,000 ppm H_2 .

The behavior of the Cu-Beta catalyst alone was also examined. Prior to these experiments the catalyst was pretreated at 550 °C with 8% O_2 to clean the surface. The NH_3 storage capacity was measured using an ammonia temperature programmed desorption (TPD) experiment in which the catalyst was exposed to 500 ppm NH_3 and 2% H_2O at 150 °C for 30 min. The sample was then flushed with argon (50 min). This was followed by a temperature ramp to 550 °C (10 °C/min). The ammonia oxidation was measured using an inlet gas composition of 500 ppm NH_3 , 8% O_2 and 2% H_2O . The temperature was increased stepwise (15 min at each step) from 150 to 500 °C. The ammonia SCR activity was investigated in a similar experiment where the temperature was increased in steps (15 min at each step) from 150 °C to 500 °C using 500 ppm NH_3 , 500 ppm NO , 8% O_2 and 2% H_2O .

3. Results and discussion

3.1. Comparison of the NSR catalyst with the NSR + SCR system

Lean/rich cycling experiments were performed over the single Pt/Ba/Al catalyst and over the combined NSR and SCR system

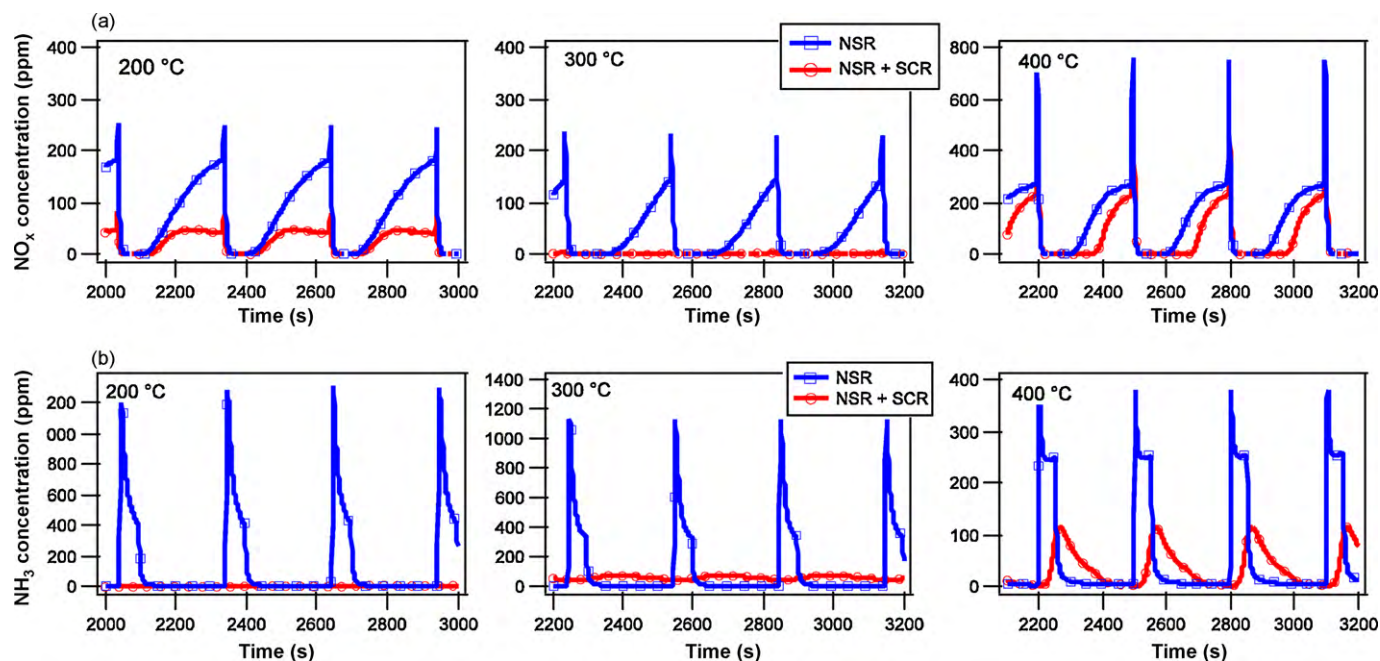


Fig. 1. Measured (a) NO_x and (b) NH_3 concentrations at 200 °C, 300 °C, and 400 °C over the single NSR catalyst and over the combined NSR and SCR arrangement. The catalysts were exposed to 300 ppm NO, 8% O_2 , 3% H_2O and 3% CO_2 during the lean period and to 300 ppm NO, 16,000 ppm H_2 , 3% H_2O and 3% CO_2 during the rich period.

at 200 °C, 300 °C, and 400 °C. Ten cycles were performed and the results from the three last cycles, in which cyclic steady state is reached, are shown in Fig. 1. The catalysts were exposed to 300 ppm NO, 8% O_2 , 3% H_2O , and 3% CO_2 during the lean period and to 300 ppm NO, 16,000 ppm H_2 , 3% H_2O , and 3% CO_2 during the rich period. The lean periods were 4 min long and the rich periods were 1 min long. When examining the results from the Pt/Ba/Al catalyst it can be seen that some of the NO_x in the feed is stored over the catalyst during lean conditions. When the gas mixture is switched into rich conditions a release of NO is initially observed and after this both the NO_x in the inlet gas feed as well as the NO_x stored is reduced. Furthermore, a significant amount of NH_3 is formed over the Pt/Ba/Al catalyst in the rich periods, as well as N_2O (see Fig. 7) and N_2 (not measured in this study). Fig. 1 clearly shows that the outlet NO_x concentration is reduced when placing an SCR catalyst downstream the NSR catalyst. This is observed at all temperatures examined. Since SCR catalysts effectively stores NH_3 [14,21] it is suggested that the ammonia formed over the Pt/Ba/Al catalyst during rich conditions is adsorbed on the Fe-beta sample. When the gas mixture is switched to lean conditions, the NO_x that is not trapped by the NSR catalyst reacts with the ammonia stored on the SCR catalyst. Hence, for the combined NSR and SCR system NO_x is removed via two routes during lean conditions: adsorption on the Pt/Ba/Al catalyst and reaction with NH_3 on the Fe-beta catalyst. Consequently, the outlet NO_x concentration is lower for the arrangement with the NSR and SCR catalysts in series compared to a single NSR catalyst. This explanation is in agreement with previous studies [14–16].

When analyzing the results from the experiments conducted at 200 °C, it is observed that the NO_x signal from the combined system is consistently lower throughout the lean periods. At the end of the lean period, just before the switch to rich conditions, the NO_x concentration from the combined NSR and SCR system is 40 ppm. The corresponding value from the NSR catalyst is 180 ppm. The best performance of the Pt/Ba/Al catalyst and the combined system is observed at 300 °C. When analyzing the single NSR catalyst it can be seen that there is a complete capture of NO_x for approximately 70 s and the NO_x concentration reached before switching to rich condi-

tions is 142 ppm. The maximum NO_x storage capacity of Pt/Ba/Al catalyst has been reported to occur at 300–400 °C [10,22–24]. At 300 °C the combined NSR and SCR system shows an exceptionally good NO_x removal efficiency; almost no NO_x is leaving the system. The reason for the excellent behavior of the combined system is discussed in Section 3.3. Fig. 1 also shows that the combined system performs better than the single NSR catalyst at 400 °C. It can be seen that there is a complete capture of NO_x for approximately 50 s for the NSR catalyst and for almost 120 s for the combined system. At the end of the lean periods the NO_x concentration is 272 ppm for the single catalyst and 235 ppm for the dual catalyst arrangement.

The outlet ammonia concentration from the systems investigated is also shown in Fig. 1. It can be seen that a large amount of ammonia is formed over the NSR catalyst. The NH_3 concentration reaches 1314 ppm during rich conditions over the NSR catalyst at 200 °C and 1140 ppm at 300 °C. A lower NH_3 concentration is observed at 400 °C; the maximum concentration reaches only 380 ppm at this temperature. The ammonia peak above the inlet NO_x concentration comes from the NO_x stored in the previous lean period. As the NO_x that was stored in the previous lean period is depleted, the NH_3 concentration decreases and ammonia is formed from the inlet NO_x . The reason for the lower ammonia peak at 400 °C is that the adsorbed NO_x species desorb more quickly from the catalyst at higher temperatures when switching to rich conditions and less NH_3 can therefore be formed. It can also be seen that the NH_3 concentration reaches a stationary value at the end of the rich periods at 400 °C. At this stage a large part of the incoming NO_x is converted into NH_3 over the NSR catalyst. It can be concluded that the amount of ammonia formed depends on the length of the rich period.

From Fig. 1 it is clear that the ammonia slip is significantly reduced when placing an SCR catalyst downstream a Pt/Ba/Al catalyst while performing NO_x storage and reduction cycles. Maximum concentrations of 15 and 78 ppm are observed at 200 °C and at 300 °C, respectively. The lower NH_3 concentration from the combined system is due to the adsorption of ammonia over the SCR catalyst, as mentioned above. In contrast to the experiments performed over the single NSR catalyst, the ammonia signal obtained

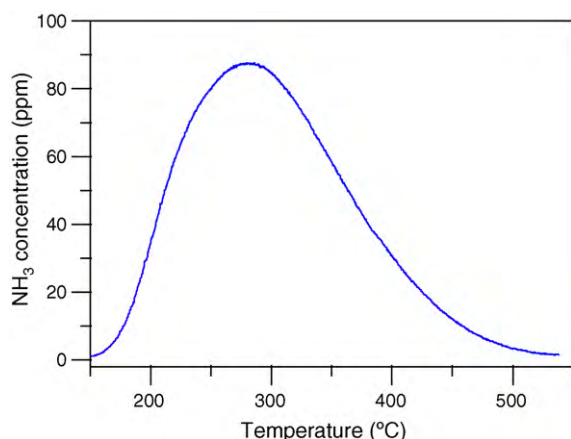


Fig. 2. Desorption of ammonia in a TPD experiment over the Fe-beta sample. The catalyst was exposed to 500 ppm NH_3 and 2% H_2O at 150 °C for 30 min and then flushed with argon before the heating ramp began (10 °C/min).

over the combined system at 400 °C during the lean/rich cycling is higher than the ammonia signal at the lower temperatures; the maximum ammonia concentration observed is 143 ppm. Hence, the opposite trend is observed for the combined NSR and SCR system. Since the difference in ammonia concentration between the two catalyst configurations is decreasing with temperature (i.e. compare 1314 ppm with 15 ppm at 200 °C and 380 ppm with 143 ppm at 400 °C), it is clear that the amount of NH_3 stored over the Fe-beta catalyst is lower at higher temperatures. In order to confirm this, the NH_3 storage capacity of the SCR catalyst was studied by means of a temperature programmed desorption (TPD) experiment in which the catalyst was exposed to 500 ppm NH_3 and 2% H_2O at 150 °C for 30 min. The sample was then flushed with argon to desorb weakly bound molecules before the heating ramp began (10 °C/min). Fig. 2 shows the result from the heating ramp. Ammonia starts to desorb almost immediately when the temperature is raised and the maximum NH_3 concentration is reached at about 300 °C. Above 300 °C the NH_3 concentration decreases, because ammonia storage is lower at higher temperatures. This is in accordance with other studies in which adsorption of ammonia over zeolites has been investigated [25,26]. Consequently, the lower ammonia concentration observed over the combined system at 200 °C and 300 °C is due to the higher adsorption capacity of the Fe-beta catalyst at low temperatures. The amount of NH_3 stored on the SCR sample also depends on the length of the rich period since more NH_3 will be formed over the NSR catalyst if the rich period is extended.

3.2. Activity of the Fe-beta catalyst

Experiments over the single Fe-beta sample was performed in order to investigate the reactivity of the SCR catalyst in the combined NSR and SCR system. The result from an ammonia oxidation experiment is shown in Fig. 3. The Fe-beta catalyst was exposed to 500 ppm NH_3 , 8% O_2 , and 2% H_2O while the temperature was increased in steps of 50 °C from 150 °C to 500 °C. It can be seen that ammonia desorbs from the sample every time the temperature is increased and the desorption peaks decrease with temperature. Ammonia starts to oxidize at 300 °C. Above that temperature more NH_3 is oxidized as the temperature is increased. At 500 °C the conversion is almost 50%.

The SCR activity of the Fe-beta catalyst was studied by exposing the catalyst to 500 ppm NH_3 , 500 ppm NO , 8% O_2 , and 2% H_2O at 150 °C for 15 min and then stepwise increasing the tempera-

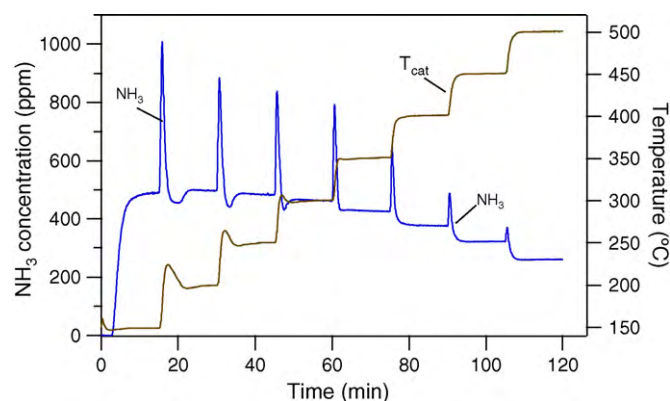


Fig. 3. Ammonia oxidation experiment over the Fe-beta sample. The catalyst was exposed to 500 ppm NH_3 , 8% O_2 , and 2% H_2O . The temperature was increased stepwise (50 °C) from 150 °C to 500 °C.

ture to 500 °C. The SCR activity is low at 150 °C but increases with temperature and at 300 °C the conversion of NH_3 is 100%.

3.3. NO_x removal efficiency and product yield

The NO_x removal efficiency of both the single NSR catalyst and the combined NSR and SCR arrangement is calculated over the three last cycles presented in Fig. 1 according to

$$\text{NO}_{x,\text{removal efficiency}} = \left(\frac{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{x,\text{in}}} \right) \times 100, \quad (1)$$

and the results are shown in Fig. 5. It can be seen that the combined NSR and SCR arrangement is very efficient with a NO_x removal efficiency ranging from 75% to 99.5%. The corresponding values for the NSR catalyst are 56–86%. At 200 °C the addition of an SCR catalyst enhances the NO_x removal efficiency the most. Both catalyst configurations perform the best at 300 °C. Actually, the combined NSR and SCR system exhibit a remarkably high NO_x removal efficiency of 99.5% at this temperature and as pointed out earlier almost no NO_x is leaving the system (see Fig. 1). There are several factors that contribute to the behavior of the combined system: the NO_x storage and reduction capacity of the NSR system, NH_3 storage capacity of the SCR catalyst and its reactivity. A number of reasons can be attributed to the excellent performance of the combined system at 300 °C. In Fig. 5 it can be seen that the NO_x removal efficiency of the single NSR catalyst is the highest at 300 °C. This is due to that the optimum storage temperature for the Pt/Ba/Al catalyst occurs at 300 °C (see Fig. 1) but also due to a high reduction capacity of

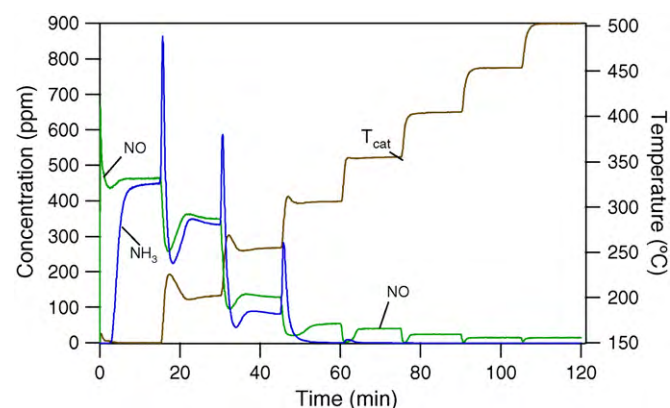


Fig. 4. Measured NO and NH_3 concentrations from an SCR activity experiment over the Fe-beta sample. The catalyst was exposed to 500 ppm NH_3 , 8% O_2 , and 2% H_2O . The temperature was increased stepwise (50 °C) from 150 °C to 500 °C.

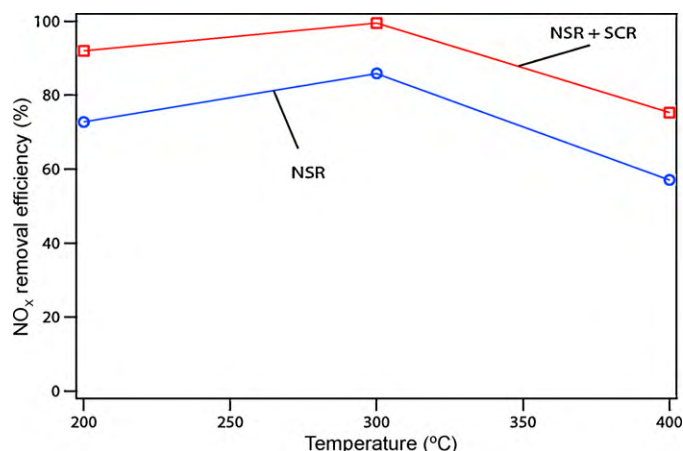


Fig. 5. NO_x removal efficiency calculated from the three last lean/rich cycles conducted over the single NSR catalyst and over the combined NSR and SCR arrangement. The catalysts were exposed to 300 ppm NO, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and to 300 ppm NO, 16,000 ppm H₂, 3% H₂O and 3% CO₂ during the rich period.

the sample at this temperature. The amount of NO_x that is released when switching from lean to rich conditions is low and the NO_x concentration is quickly reduced to zero. The performance of the SCR catalyst also contributes to the high NO_x removal efficiency of the combined system. Lean/rich cycling experiments were conducted over the Fe-beta catalysts (not shown here) and it was observed that only minor amounts of NO_x was stored at all temperatures examined (200–400 °C). It can therefore be concluded that the increase in the NO_x removal efficiency of the combined system is not due to adsorption of NO_x over the SCR catalyst. The TPD experiment and the low concentration of ammonia from the combined system (shown in Fig. 1b) indicate that the ammonia storage capacity of the SCR catalyst is high at 300 °C. In addition, the NO_x conversion during SCR with NO and NH₃ is very high at 300 °C (Fig. 4). Moreover, NO is oxidized to NO₂ over the Pt/Ba/Al catalyst and it is therefore expected that the fast SCR reaction occur over the Fe-beta sample. Since more NO₂ is produced at 300 °C than at 200 °C and 400 °C (not shown here) it is likely that the NO_x removal efficiency of the combined system is improved by the fast SCR reaction at 300 °C. Forzatti and Lietti [15] also observed a high NO_x removal efficiency at 300 °C and explained this with the high NO_x uptake of the NSR catalyst. Both the combined NSR and SCR arrangement and the single NSR catalyst perform the worst at 400 °C with NO_x removal efficiencies of 75% and 57%, respectively. This is due to that less NO_x is stored over the Pt/Ba/Al catalyst which results in a higher NO_x slip from this catalyst. The higher NO_x slip in combination with the lower amount NH₃ stored over the Fe-beta catalyst results in a decrease in the NO_x removal efficiency. Ammonia oxidation over the Fe-beta sample also contributes to the lower NO_x removal efficiency at this temperature as is shown in Fig. 3. The NH₃ and the N₂ yields are presented in Table 1 and Fig. 6 and are calculated over the three last cycles presented in Fig. 1 according to

$$S_{\text{NH}_3} = \frac{\text{NH}_{3,\text{out}}}{\text{NO}_{x,\text{in}}} \times 100 \quad (2)$$

Table 1
NH₃ yield at 200, 300, and 400 °C.

Catalyst arrangement	200 °C (%)	300 °C (%)	400 °C (%)
NSR	44	34	19
NSR + SCR	3	21	12

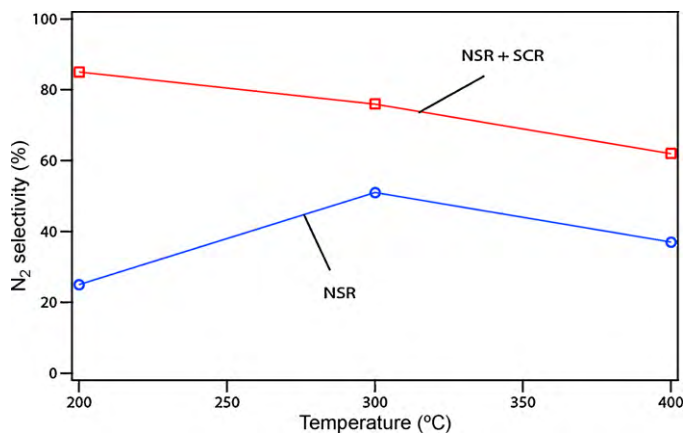


Fig. 6. N₂ yield calculated from the three last lean/rich cycles conducted over the single NSR catalyst and over the combined NSR and SCR arrangement. The catalysts were exposed to 300 ppm NO, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and to 300 ppm NO, 16,000 ppm H₂, 3% H₂O and 3% CO₂ during the rich period.

$$S_{\text{N}_2} = \frac{\text{NO}_{x,\text{in}} - (\text{NO}_{x,\text{out}} + \text{NH}_{3,\text{out}} + 2\text{N}_2\text{O}_{\text{out}})}{\text{NO}_{x,\text{in}}} \times 100 \quad (3)$$

Nitrogen is not measured in the experiments performed in this work, thus the N₂ yield is obtained as a difference between the inlet NO_x concentration and the outlet concentrations of the products formed, as can be seen from the equation above. It is clear that the ammonia yield of the combined system, which ranges between 3% and 21%, is significantly lower than the yield of the NSR catalyst, which ranges between 19% and 44%. The highest NH₃ yield of the NSR catalyst is achieved at 200 °C and it decreases when the temperature is increased. In contrast to the single NSR catalyst, the ammonia yield of the combined system is the lowest at 200 °C. At this temperature the yield is as low as 3%. As can be seen in Fig. 1 a very low ammonia concentration is observed at 200 °C, which is due to the high adsorption capacity of the Fe-beta catalyst at low temperatures, as pointed out earlier. The highest ammonia yield is achieved at 300 °C ($S_{\text{NH}_3} = 21\%$) for the combined system. Still, the adsorption capacity of the Fe-beta catalyst is high at 300 °C. However, due to the large amount of ammonia stored the catalyst is saturated and ammonia will slip through the system during both lean and rich conditions. This occurs also at 200 °C but a lower amount of NH₃ is observed in the gas phase, due to the higher ammonia storage capacity at lower temperatures. Even though the highest concentration of ammonia from the combined system is observed at 400 °C (see Fig. 1), the ammonia yield is only 12% at this temperature. The reason for this is that the ammonia concentration is zero during some parts of both the lean and rich periods at this temperature, which is attributed to reaction between NH₃ adsorbed on the SCR catalyst and NO_x or O₂ from the feed during lean conditions and the adsorption of NH₃ during rich conditions. The ammonia slip from the combined system can be reduced by shortening the rich period.

A significant increase in the N₂ yield is observed when an SCR catalyst is placed downstream an NSR catalyst. The largest difference between the two catalyst arrangements is identified at 200 °C, where the N₂ yield is as high as 85%. As mentioned above the N₂ yield is obtained as a difference between the inlet NO_x concentration and the outlet concentrations of the products formed. A high amount of NH₃ is formed over the NSR catalyst at 200 °C (see Fig. 1) which results in a low N₂ yield according to Eq. (3). Since almost all ammonia is adsorbed over the Fe-beta sample in the combined system and further reacting to N₂ in the lean period a much higher N₂ yield is achieved at this temperature for the combined system. Hence, the reason for the high N₂ yield is due to the high capac-

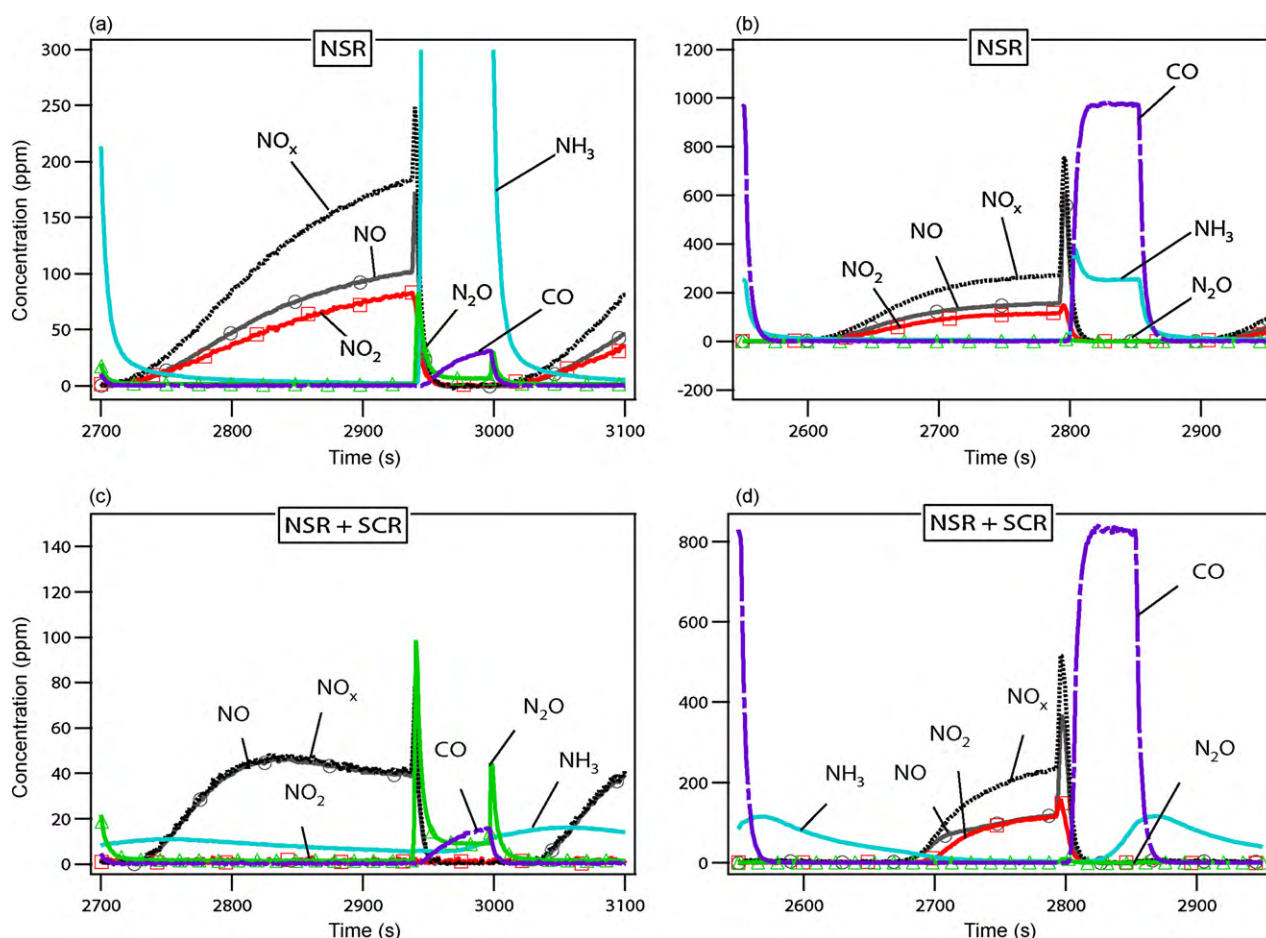


Fig. 7. Outlet NO, NO₂, NO_x, N₂O, NH₃, and CO concentrations over the single NSR catalyst at (a) 200 °C and at (b) 400 °C and over the combined NSR and SCR configuration at (c) 200 °C and at (d) 400 °C. The catalysts were exposed to 300 ppm NO, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and to 300 ppm NO, 16,000 ppm H₂, 3% H₂O and 3% CO₂ during the rich period.

ity of adsorbing NH₃ over the Fe-beta catalyst. The lowest N₂ yield is achieved at 400 °C for the combined system. However, the yield at this temperature is still higher than the highest yield achieved by the single NSR catalyst. The results presented here are in line with the study performed by Forzatti and Lietti [15], who found that the N₂ production increased with decreasing temperature. For the single NSR catalyst there is an optimum temperature for the yield to N₂. The highest yield is achieved at 300 °C. This is mainly ascribed to the high storage capacity of the Pt/Ba/Al catalyst at this temperature since the outlet NO_x concentration is low during the lean periods and the N₂ yield is obtained as a difference between inlet and outlet concentrations.

3.4. Products formed over Pt/Ba/Al and the combined NSR + SCR system

Fig. 7 shows all components formed at 200 °C and 400 °C during the last cycle from the lean/rich cycling experiments of the single Pt/Ba/Al catalyst and of the combined NSR and SCR system. The catalysts were exposed to 300 ppm NO, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and to 300 ppm NO, 16,000 ppm H₂, 3% H₂O and 3% CO₂ during the rich period. The lean periods were 4 min long and the rich periods were 1 min long. In the beginning of the lean period all NO_x in the gas feed is stored over the Pt/Ba/Al catalyst. When the lean period continues the storage capacity of the NSR catalyst decreases and a low concentration of NO_x is observed in the outlet of this catalyst. Since the NO_x concentration out from the NSR catalyst is so low all NO_x can be reduced by the am-

monia stored over the SCR catalyst. Hence, the NO_x concentration observed over the combined system remains at 0 ppm for a longer while. As the trapping capacity of the NSR catalyst continues to decrease the NO_x signal out from the NSR catalyst increases. The SCR catalyst is not able to reduce all NO_x and the NO_x signal out from the combined system is therefore also increasing. An interesting feature is observed over the combined system during the lean period at 200 °C. The NO_x concentration decreases after 130 s of the lean period. Since this characteristic only is observed over the combined system it is concluded that this feature is attributed to the SCR catalyst. When the lean period continues the amount of ammonia stored in the Fe-beta catalyst decreases due to the SCR reaction between NO_x and ammonia adsorbed. It is well known that ammonia can inhibit the SCR reaction, especially over iron containing zeolites [27]. Since we use an Fe zeolite in this work also we suggest the lower amount of ammonia adsorbed in the SCR catalyst enhances the SCR activity which results in a lower NO_x concentration. This feature is not observed at 400 °C, which probably is due to that the amount of ammonia stored is much lower at this temperature. Due to the NO oxidation occurring over the Pt/Ba/Al sample, both NO and NO₂ are observed in the effluent gas from this catalyst. When comparing the NO and NO₂ concentrations from the NSR catalyst with the concentrations from the combined system at 200 °C, it can be seen that both the NO concentration and the NO₂ concentration from the combined NSR and SCR system are lower. Actually no NO₂ is observed over the combined system. Hence, it can be concluded that the SCR catalyst consumes all NO₂ and some of the NO. Therefore, the fast SCR reaction, where equal amounts of NO and

NO_2 react with ammonia and forms N_2 and H_2O , is likely to occur. Since NO oxidation also occurs at 400°C over the Pt/Ba/Al catalyst, the fast SCR reaction is expected to take place over the combined system at this temperature as well. However, not all NO_2 is consumed at this temperature, probably due to less available ammonia due to the low ammonia storage at high temperature.

A large amount of ammonia is formed over the NSR catalyst during the rich period at 200°C . The ammonia concentration is above 1100 ppm at this temperature, which can be seen in Fig. 1. In Fig. 7 a magnification is done, which is why the high level of ammonia is not visible (it is not two ammonia peaks, it is the start and end of the ammonia peak that is visible at this high magnification). But almost no ammonia is observed during lean conditions; only a small amount can be seen which is the tailing from the previous rich period. However, a low amount of ammonia is observed both during lean and rich conditions over the combined system at this temperature. A lot of ammonia is stored over the Fe-beta sample at 200°C and 300°C (the maximum NH_3 concentration produced over the Pt/Ba/Al catalyst is higher than 1100 ppm at 200°C and 300°C , see Fig. 1) and not all of it will be consumed during lean conditions. This means that the Fe-beta catalyst will not be completely regenerated from NH_3 and ammonia will therefore accumulate over the sample. This is observed by a steadily increase in the outlet NH_3 concentration at both 200°C and 300°C when examining all ten lean/rich cycles (not shown here). Hence, the ammonia concentration does not decrease to zero during lean conditions at low temperatures for the combined system. At 400°C , on the other hand, the ammonia concentration decreases slowly during lean conditions until it reaches 0 ppm. The NH_3 concentration stays at 0 ppm for approxi-

mately 30 s during the rich period before the SCR catalyst becomes saturated and NH_3 is observed in the effluent gas. As mentioned earlier the amount of ammonia adsorbed over the SCR catalyst is lower at 400°C than at 200°C and 300°C . Hence, at 400°C the Fe-beta catalyst can be regenerated from NH_3 during lean conditions by the SCR reaction with NO_x . It is also possible that ammonia is oxidized by O_2 present in the gas phase during lean conditions at this temperature. As mentioned above, almost no NH_3 is observed from the Pt/Ba/Al catalyst during lean conditions at the temperatures examined. However, ammonia is always present in the beginning of the lean period in the experiments performed over the combined NSR and SCR system. The presence of ammonia must therefore be ascribed to the performance of SCR catalyst. It has been shown that as the ammonia is shut off in NH_3 TPD experiments over a Cu-ZSM-5 sample, the loosely bound ammonia desorbs from the catalyst and it takes several minutes before the ammonia signal decreases to 0 ppm [21]. Hence, the reason for the occurrence of NH_3 during lean conditions is that ammonia desorbs from the adsorption sites of the Fe-beta catalyst when ammonia no longer is present in the effluent of the NSR catalyst (i.e. in the feed to the SCR catalyst).

Nitrous oxide is formed over the Pt/Ba/Al catalyst at 200°C during rich conditions. The N_2O concentration increases to a maximum and the concentration then falls off to a low steady state level. Formation of N_2O during rich conditions, when using hydrogen as reductant, has been observed earlier over NSR catalysts [3–5,10]. It has been reported that the formation is favored at low temperatures [10]. This trend is also valid in the experiments performed in this study, i.e. N_2O is formed at 200°C but not at 400°C (see Fig. 7a and b). In Fig. 7a a second N_2O peak is observed when switching

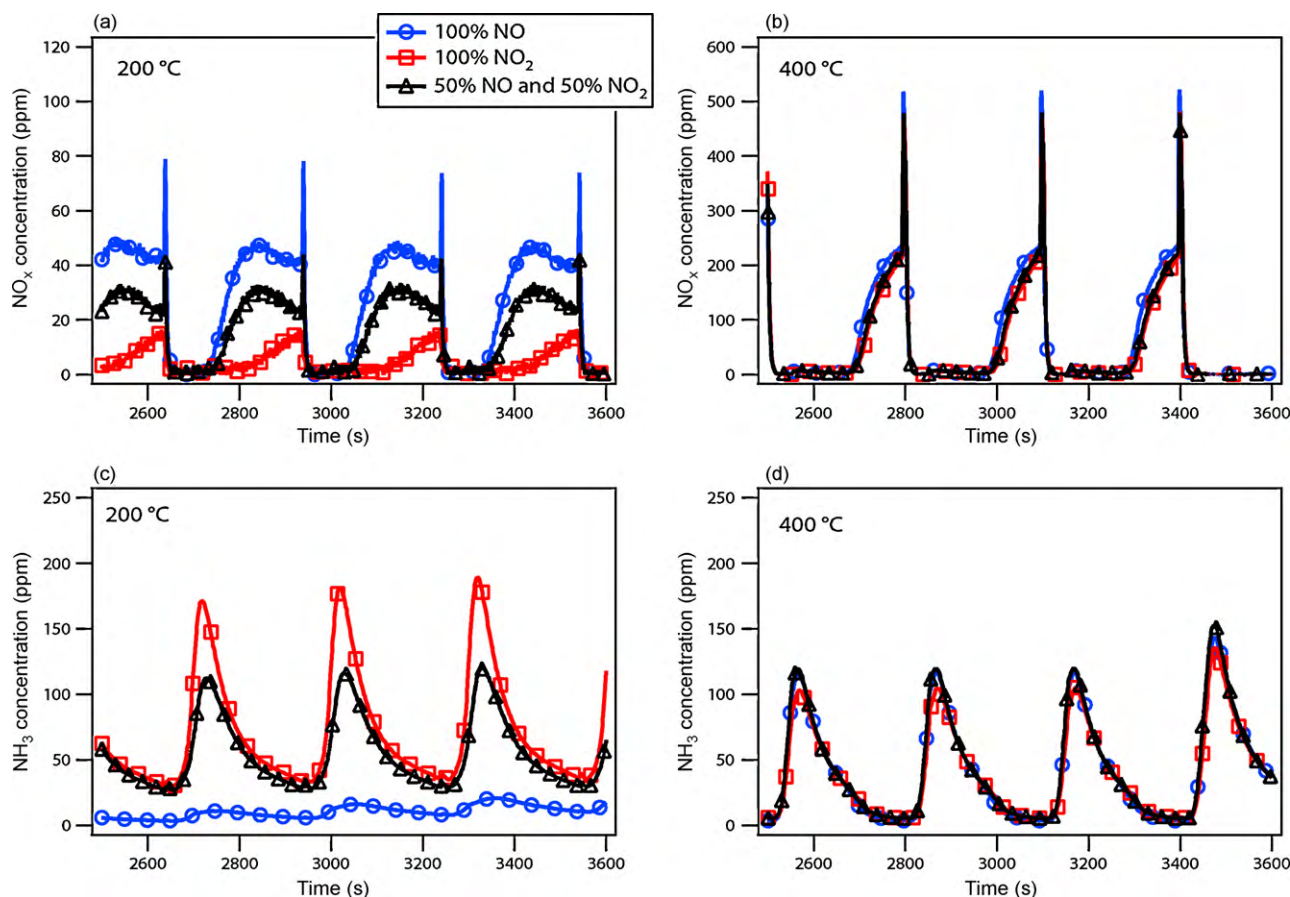


Fig. 8. Measured NO_x and NH_3 concentrations at (a) and (c) 200°C and at (b) and (d) 400°C from experiments with varying NO_x source over the combined NSR and SCR system. The inlet feed concentration contained 300 ppm NO_x , 8% O_2 , 3% H_2O and 3% CO_2 during the lean period and 300 ppm NO_x , 16,000 ppm H_2 , 3% H_2O and 3% CO_2 during the rich period. The examined NO_x source was either 300 ppm NO , 300 ppm NO_2 or 150 ppm NO and 150 ppm NO_2 .

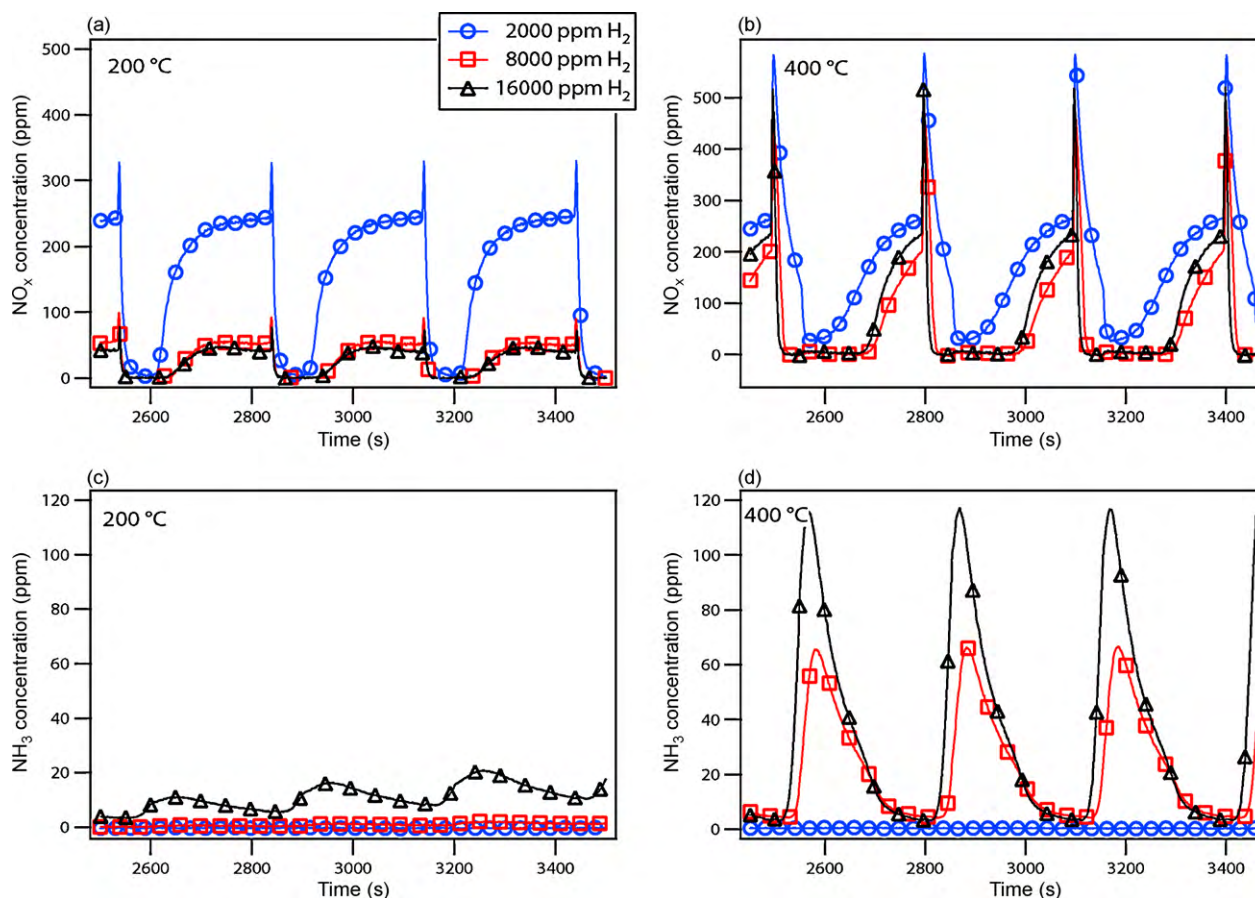


Fig. 9. Measured NO_x and NH₃ concentrations at (a) and (c) 200 °C and at (b) and (d) 400 °C from experiments with varying concentrations of H₂ over the combined NSR and SCR system. The inlet feed concentration contained 300 ppm NO, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and 300 ppm NO, varying H₂ concentration, 3% H₂O and 3% CO₂ during the rich period. The examined H₂ concentration was either 2000, 8000, or 16,000 ppm H₂.

from rich to lean conditions. This feature has been observed in our previous study performed over both Pt/Ba/Al and Pt/Al catalysts [22]. We suggested that the second N₂O peak appears due to that hydrogen species are present on the surface during rich conditions. These species react with the incoming NO_x in the initial part of the lean period and as a result N₂O can be formed. The same characteristic of the N₂O formation, with similar concentrations, is observed over the combined NSR and SCR system as can be seen in Fig. 7c and d. We therefore suggest that N₂O is formed over the NSR catalyst in the combined system.

Furthermore, a small amount of CO is formed over the NSR catalyst during rich conditions at 200 °C by the reverse water gas shift reaction, where H₂ and CO₂ react and produce H₂O and CO. Carbon monoxide is also observed in the effluent gas from the combined system but with a lower concentration. Additionally, a higher CO concentration is observed over both systems at 400 °C compared to at 200 °C. At this temperature as much as 980 ppm CO is formed over the NSR catalyst and the concentration observed over the combined system is 840 ppm.

3.5. Effect of the NO/NO₂ ratio

The effect of the inlet NO/NO₂ ratio on the performance of the combined NSR and SCR system was investigated at 200 °C, 300 °C, and 400 °C. The catalysts were exposed to 300 ppm NO_x, 8% O₂, 3% H₂O and 3% CO₂ during the lean period and to 300 ppm NO_x, 16,000 ppm H₂, 3% H₂O and 3% CO₂ during the rich period. The inlet NO_x concentrations were either 300 ppm NO, 300 ppm NO₂ or 150 ppm NO and 150 ppm NO₂. Fig. 8 shows the results from

experiments performed at 200 °C and 400 °C. It can be seen that the NO_x removal efficiency is increased at 200 °C (Fig. 8a) when NO₂ is present in the gas feed. The highest amount of NO_x is removed when the gas feed contains only NO₂ as the NO_x source. In addition, the largest ammonia slip is emitted in this experiment (see Fig. 8c). The same experiments were also performed over the single NSR catalyst (not shown here) and they showed that the amount of NO_x stored at 200 °C was significantly increased when NO₂ was present in the gas feed. But the amount of ammonia produced was not affected by the type of NO_x source. In the combined system the SCR catalyst is consequently exposed to a lower amount of NO_x when NO₂ is present in the gas feed and more NH₃ will therefore be emitted. We suggest that the increase in the NO_x removal efficiency when NO₂ is present in the feed is mostly due to the increase in the amount of NO_x stored over the NSR catalyst. Furthermore, when NO is present in the feed, only NO is observed in the effluent. Since some of the NO is oxidized into NO₂ over the Pt/Ba/Al catalyst it can be concluded that all NO₂ is consumed over the SCR catalyst. Consequently, it is likely that the fast SCR reaction occur over the Fe-beta sample, as mentioned earlier. On the other hand, when 100% NO₂ is used as the NO_x source, only NO₂ is observed in the effluent stream of the combined system. Some of the NO₂ is dissociated into NO over the Pt/Ba/Al catalyst but the SCR catalyst is mostly exposed to NO₂. We suggest that the fast SCR reaction consumes all NO produced over the Pt/Ba/Al catalyst and the excess NO₂ is observed in the effluent. Some NO₂ is probably also consumed by the NO₂-SCR reaction.

In Fig. 8b and d it can be seen that there is no difference between the experiments conducted at 400 °C. Similar NO_x and NH₃ concentrations are observed from all experiments. This is due to that

the thermodynamic levels of the NO oxidation reaction is reached over the Pt/Ba/Al catalyst at 400 °C and the same NO/NO₂ ratio is achieved over this catalyst regardless of the amount of NO or NO₂ in the inlet. The amount of NO_x stored and the reduction products formed over the NSR catalyst is the same for all experiments and the SCR catalyst will therefore be exposed to the same gas feed.

3.6. Effect of the H₂ concentration

The influence of the hydrogen concentration on the performance of the combined NSR and SCR system was studied at 200 °C, 300 °C, and 400 °C. The catalysts were exposed to 300 ppm NO and 8% O₂ during lean conditions and 300 ppm NO and varying concentrations of hydrogen; 3% H₂O and 3% CO₂ were always present in the gas feed. The hydrogen concentrations studied were 2000, 8000, and 16,000 ppm. Fig. 9 shows the results from experiments performed at 200 °C and 400 °C and it can be seen that the amount of NO_x removed is influenced by the amount of hydrogen in the rich period. When the hydrogen concentration is increased at 200 °C the amount of NO_x removed is increased. The combined system performs poor when only 2000 ppm H₂ is used. There are two reasons for the low performance. The first reason is that the amount of hydrogen is not enough to regenerate the Pt/Ba/Al catalyst at this temperature and consequently, the NO_x storage performance is low. The second reason is that the amount of NH₃ from the NSR catalyst is very low. This is showed in [10] where we performed NSR cycles, with 300 ppm NO and 2000 ppm H₂ in the rich period, over the same Pt/Ba/Al catalyst as used in this study. In these experiments it took approximately 2 min before NH₃ was observed in the gas phase. However, the lean period was 10 min and the rich period was 5 min. But it is expected that the amount of NH₃ from the NSR catalyst is low also for the conditions used in this study. We suggest that the amount of NH₃ that reaches the SCR catalyst is low and the SCR activity is therefore most likely small. For these conditions the improvement of the NO_x removal efficiency is minor when adding the SCR catalyst. This is confirmed in Fig. 9c, where it can be observed that the ammonia concentration is zero during the lean/rich cycling. When 8000 ppm H₂ or 16,000 ppm H₂ is used the NO_x removal capacity is high. The lowest amount of NO_x is observed when 16,000 ppm H₂ is used; however, the difference between the NO_x signals is small. A very low ammonia concentration is observed in the effluent when 8000 ppm H₂ is used and the concentration of ammonia from the experiment when 16,000 ppm H₂ is used is higher. However, also for this experiment the ammonia concentration is very low.

A different trend of the NO_x removal capacity is observed at 400 °C. An optimum hydrogen concentration seems to exist at this temperature. The NO_x removal capacity is the lowest when 2000 ppm H₂ is used and the highest when 8000 ppm H₂ is used. When increasing the H₂ concentration further, the NO_x removal capacity decreases. The amount of NO_x stored over the Pt/Ba/Al is probably higher when a higher hydrogen concentration is used due to a more complete regeneration of the storage sites. Therefore the better NO_x removal efficiency is likely connected to the reactions occurring over the SCR catalyst. Fig. 9d shows the ammonia concentrations from the experiments conducted at 400 °C and it can be seen that the highest NH₃ concentration is observed for the highest hydrogen concentration. A better NO_x removal capacity and a lower NH₃ slip are achieved when 8000 ppm H₂ is used. When the higher hydrogen concentration is used a high amount of ammonia is produced over the Pt/Ba/Al sample and more NH₃ is adsorbed over the Fe-beta catalyst. As discussed earlier a high amount of ammonia adsorbed inhibits the SCR reaction. Consequently, a lower hydrogen concentration will likely enhance the SCR activity.

4. Conclusions

In this work the reduction of NO_x over the combined NSR and SCR system was investigated. The outlet NO_x and NH₃ concentrations are significantly reduced when an SCR catalyst is placed downstream an NSR catalyst. The ammonia formed over the Pt/Ba/Al catalyst during rich conditions is effectively stored in the SCR catalyst which results in a lower NH₃ slip. When the gas mixture is switched to lean conditions, NO_x is removed via two routes: adsorption on the Pt/Ba/Al catalyst and reaction with NH₃ on the Fe-beta catalyst. Only minor amounts of NO_x were stored over the SCR catalyst. Due to that oxidation of NO into NO₂ occurs over the Pt/Ba/Al catalyst, it is suggested that the fast SCR reaction takes place over the Fe-beta sample. An exceptionally high NO_x removal efficiency of 99.5% is achieved at 300 °C, which is the optimum temperature for NO_x removal of the combined system. The lowest NH₃ and the highest N₂ yield are observed at 200 °C due to the high ammonia adsorption capacity of the SCR catalyst at this temperature. The NO_x removal efficiency increases at low temperatures when NO₂ is present in the feed. This effect is mainly attributed to the increase in the amount of NO_x stored over the Pt/Ba/Al sample. It is also concluded that the amount of NO_x removed is influenced by the amount of hydrogen in the rich period. A higher hydrogen concentration yields a larger amount of ammonia formed over the Pt/Ba/Al catalyst. At low temperatures the higher amount of ammonia results in a higher SCR activity with a higher NO_x removal efficiency as a consequence. At high temperatures, an optimum hydrogen concentration is observed, due to ammonia inhibition of the SCR reaction at higher hydrogen concentrations.

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